PATENT SPECIFICATION (11) 1 564 128

43

1 564 128

(21) Application No. 43312/76 (22) Filed 19 Oct. 1976

(23) Complete Specification Filed 15 Nov. 1977

(44) Complete Specification Published 2 Apr. 1980

(51) INT. CL.^{3} B05D 7/16 3/00
B32B 15/08 27/34

(52) Index at Acceptance
B2E 1327 1329 FE

(19)

THE PATENT OFFICE LONDON

(72) Inventors: ROGER JOHN DOREY
GABRIEL GAVRIELIDES

(54) METHOD OF PREPARING METAL SURFACES

(71) We, UNITED GLASS LIMITED, a British company of Kingston Road, Staines, Middlesex, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the preparation of metal surfaces especially concerned with the coating of handling equipment used in the manufacture of glassware.

In the manufacture of glassware by automatic processes the molten glass issuing from the furnace is formed in the machine into the desired shape, and may then be transferred to a conveyor whence it is subsequently transferred to an annealing oven or lehr. While the glass is at an elevated temperature and is being handled on conveyors and by line transfer equipment the glass surface is extremely senstive to damage by hard or abrasive materials. Furthermore the use in the handling equipment of a material of high thermal conductivity which may cause sudden cooling of the glass surface could result in the presence of small cracks in the glass surface.

In our co-pending U.K. Application No. 49838/75 (Serial No. 1562569) we have described a rigid non-metallic composite material which may be used to replace either metal or asbestos-based materials in glassware handling devices where it is convenient to effect this change. There are, however, a number of situations where it may not be readily possible to replace metal in use, or to readily effect a change to another material. These considerations apply for example when a particular part in use requires the mechanical properties of metal. A good example of this is the conveyor belt which carries bottles from the forming machine to the annealing lehr. When hot bottles are transferred onto this conveyor belt the high thermal conductivity of the metal may cause undue cooling of the glass, leading to cracks, and for this reason it is common practice to apply a graphitic dope frequently to the conveyor belt so as to provide an intermediate layer of carbon between the glass and the metal. There are however a number of unsatisfactory features about such a process, including the need to apply the dope frequently, and the manner in which the conveyor belt thereby becomes prone to absorption of oil which is subsequently transferred to the bottles resulting in indelible marking, and in possible damage to the glass surface.

It is well known that similar considerations apply to the treatment of blank moulds used in glass forming machines, and in recent years it has been found possible to replace the frequent treatment of the moulds with graphitic dope by a single treatment with a suitable material known as a solid film lubricant. Various lubricants of this type exist, and most commonly they consist of graphite in a suitable resin base. Since the resin has to withstand a high temperature there is a limited choice available, and polyimide resins are among those in use. Thus, it is known to apply mixtures of polyimide and graphite to the surfaces of blank moulds to be used for hot glass contact as a means of providing lubrication in replacement of graphitic dope.

However, the application of these solid film lubricants to the blank moulds is carried out by an off-line process which requires application of the coating and careful curing schedules, extending over periods of several hours. to ensure that the coating is satisfactory.

For certain metallic parts which come into contact with hot glass, for example conveyor belts, it can be most impractical to carry out such a treatment, and indeed once installed the conveyor belt generally remains in position for several months or years until failure of the belt ocurs. Furthermore, removal and re-installation of the belt are time consuming jobs,

and can only be carried out during a period when the machine is idle or the moulds are being changed. These idle periods generally are of the order of one to two hours, and it would clearly be impossible to remove the belt, treat it, and re-install it within this period.

It is therefore an object of this invention to provide a method which will enable a conveyor belt or other item of metal equipment to be used for handling hot glassware to be treated *in situ* with a suitable resin-graphite system which can be cured to a satisfactory coating within the period between the manufacture of one type of glassware and another.

According to the present invention a method of preparing a metal surface to render it suitable or more suitable for contact with hot glassware comprises raising the temperature of the said surface to an extent sufficient to clean it, applying to the cleaned surface a liquid composition comprising a thermosetting polyimide resin and graphite, removing the solvent and curing the polyimide resin.

The method of the invention thus comprises four steps. In the first of these the surface to be prepared is heated to an extent sufficient to clean it. By this we mean that it should be freed of any grease that may have adhered to it. Any suitable heating means may be used for this, but we prefer a gas flame, which will rapidly raise the temperature of the surface to be prepared (e.g. the surface of a conveyor belt or a "dead plate" between communicating belts) to the temperature necessary to burn off any adhering grease or dirt. Heating the surface to temperatures of about 250°C for up to 10 minutes will normally be sufficient for this purpose.

In the second step of the process a coating composition of thermosetting polyimide resin and graphite is applied to the surface. It is applied in the form of a solution or suspension in an inert solvent, and suitably by spraying. A typical solvent is N-methyl pyrrolidone; an alternative is a mixture of N.methyl pyrrolidone and xylene. The most useful solvents are those having the lowest viscosity consistent with the ability to dissolve or suspend the resin. Suitable resins are those sold by the Monsanto Company under the trade names "Skybond 700" and "Skybond 703", and that sold by Du Pont & Co. under the trade name "Pyralin PZ-4701". These are condensation-type resins. A suitable solution or suspension comprises a solids content of 45-75% e.g. 60-70%. The ratio of polyimide: graphite in the coating material may vary within quite wide limits, ratios of 0.5 to 4:1, e.g. 1 to 4:1, being preferred. As an example, the mixture may contain 36 parts by weight N-methyl pyrrolidone, and 64 parts solids (of which 66% by weight is resin and 34% by weight is graphite). The graphite preferably has a particle size in the range 15-20μm (Hegman). The resin-graphite mixture may also contain additives such as dispersing agents and spray lubricants. An example of the former is "Nuosperse 657", sold by the Durham Chemical Group; a suitable spray lubricant is "Rhodorsil Oil 640 V100", sold by Rhone-Poulenc. (Skybond", "Nuosperse", "Rhodorsil" and "Pyralin" are trade marks).

Mixtures of resins may be used if desired, and whereas an exclusively thermosetting material will give a hard final surface coating, it is possible to achieve a more flexible final coating, such as would be suitable for a conveyor belt, by incorporating in the resin mixture a minor amount of a thermoplastic polyimide resin. Thus, for example, up to 20%, suitably 10-20%, by weight of the thermosetting resin may be replaced with thermoplastic resin to give a surface coating which has a desirable degree of flexibility but nevertheless the ability to withstand contact with the hot glass. The surface coating desirably has a thickness of 10-20μm.

It is preferred that the cleaned surface should be allowed to cool after heat treatment and before application of the resin-graphite mixture, preferably of the solvent will determine the precise temperature of application thereof and thus the temperature to which the surface should be cooled. The optimum conditions for application of the coating medium are those which will give an even layer of coating material on the surface, and if the temperature is too high the solvent will evaporate off too rapidly for this, whereas too low a temperature may result in an insufficient rate of evaporation. When using a liquid mixture in N-methyl pyrrolidone, we have found that a surface temperature of the order of 90°C to 120°C gives very satisfactory results. The resin-graphite mixture is preferably applied using a hot spray technique so as to reduce the viscosity of the resin.

After application of the solvent-based resin mixture the solvent is allowed to evaporate before proceeding to the fourth and final step, the curing of the coating.

The solvent removal step must be carried out with care. Too rapid a rate of drying will result in premature curing and blistering of the resin, while too slow a rate of drying will reduce the overall efficiency of the coating since it may not then be possible to treat the metal surface to the required extent during the changeover from one job to another. We have found that the solvent removal step is suitably carried out by heating the surface at a temperature of 120°C to 150°C while at the same time blowing air across the surface. In the case of open-mesh metal conveyors in infra-red heating element may be placed beneath the conveyor and air is blown through the conveyor from below. The inflammable solvent

vapours are thus blown away from the heating element. Under these conditions it will normally be possible to evaporate substantially all the solvent within about 20 minutes.

The final stage of the process may be achieved by mounting a suitable infra-red heating element close to the conveyor belt or other metal surface being treated, such that as the surface passes adjacent to the element the surface temperatre of the polyimide in the coating is raised to at least 250°C and preferably to about 350°C. It has been found that repeated passage of coated parts past such an element for a period of, say, up to one hour at the minimum temperature will effect a satisfactory cure of the resin. At 350°C cure may be complete within 5 to 10 minutes. Other available techniques for effecting cure of surface coating are, of course, also applicable in the method of the invention. The cured coating on the belt or other metal part thus obtained is reasonably resistant to heat and damage, resistant to the action of oil and grease, minimises damage to the hot glass through thermal shock cracking, provides lubricity to the bottles and other glassware when they slide on an off the parts as required, and does not require any maintenance by the way of doping etc., during a period of at least several days.

Although the description herein of the method of coating metal parts relates primarily to a period when the parts are not in actual use, we have found that in certain circumstances it is possible to apply and cure the coating while the part is in use. In the case of a conveyor belt, for example, all the steps described above can be carried out while the belt is simultaneously used for the transport of hot bottles. The resultant coating on the belt, however, may not have as long a life as the coating on a belt provided during an idle period of production.

The following Example is given for the purpose of illustrating the invention.

Example

A conveyor belt which carries glass bottles from the forming machine to the annealing lehr was first cleaned by passing it through a gas flame so that the surface of the metal reached a temperature of 250°C, and this treatment was maintained for ten minutes. The belt was then allowed to cool for fifteen minutes, by which time the temperature had fallen to under 100°C, and it was then sprayed with a resin mix formulated as follows:-

Pyraline PZ-4701 (44% resin solids)	585.00	parts by weight
Graphite powder Rocol X7119	257.30	" " "
Nuosperse 657 (dispersing agent)	1.2	" " "
Rhodorsil Oil 640 V100 (spraying lubricant)	0.3	" " "
Diluent MPX	156.2	" " "

(The Diluent MPX consisted of 6 parts by weight of N-methyl pyrrolidone and 4 parts by weight of xylene).

The solid content in the final formulation was 51.5% and the resin/graphite ratio was 1. The mix was produced in a ball mill to a Hegman gauge 6.5.

The mix was sprayed onto the conveyor belt at a rate of 50 gms/m^2. The belt was then passed over a 6 Kw infra-red heater, and air blown from underneath so as to remove the solvent and ensure that the belt temperature was somwhere in the range of 120-150°C. About 200 cubic feet of air per minute was required for this purpose. After fifteen minutes the air blower was turned off and the temperature of the belt allowed to increase to 300°C; this was maintained for thirty minutes after which the heater was switched off and the belt allowed to cool. The coating thickness was separately determined to be about 15 micrometers. A bottle placed upon the coated belt was found to have a static coefficient of friction of approximately 0.15, whereas a similar bottle placed upon an uncoated belt had coefficients of friction ranging from 0.25 to 0.7, depending upon the degree of oil contamination of the uncoated belt.

WHAT WE CLAIM IS:-

1. A method of preparing a metal surface comprising raising the temperature of the surface to an extent sufficient to clean it, applying to the cleaned surface a liquid composition comprising a thermosetting polyimide resin and graphite, removing the solvent and curing the polyimide resin.

2. A method as claimed in claim 1 wherein the metal surface is cleaned by heating it to a temperature of about 250°C for up to 10 minutes.

3. A method as claimed in claim 1 or 2 wherein the solvent is N-methyl pyrrolidone.

4. A method as claimed in claim 1 or 2 wherein the solvent is a mixture of N-methyl pyrrolidone and xylene.

5. A method as claimed in any of claims 1 to 4 wherein the liquid composition has a solids content of 45-75%.

6. A method as claimed in claim 5 wherein the solids content of the composition is 60-70%.

7. A method as claimed in any of claims 1 to 6 wherein the ratio of polyimide to graphite in the composition is 0.5 to 4:1.

8. A method as claimed in claim 7 wherein the said ratio is 1 to 4:1.

9. A method as claimed in any of claims 5 to 8 wherein the composition comprises, by weight, 36 parts N-methyl pyrrolidone and 64 parts solids of which 66% is polyimide resin and 34% is graphite.

10. A method as claimed in any of claims 1 to 9 wherein the graphite has a particle size of 15-20μm (Hegman).

11. A method as claimed in any of claims 1 to 10 wherein the thermosetting polyimide resin is replaced with up to 20% by weight of a thermoplastic polyimide resin.

12. A method as claimed in any of claims 1 to 11 wherein the liquid composition is applied to the metal surface when the latter is at a temperature of 90 to 120°C.

13. A method as claimed in any of claims 1 to 12 wherein the solvent is removed by heating the metal surface to a temperature between 120 and 150°C whilst blowing air across it.

14. A method as claimed in any of claims 1 to 13 wherein the polyimide resin is cured by heating it to a temperature of at least 250°C.

15. A method as claimed in claim 14 wherein the resin is cured by heating it to a temperature of about 350°C.

16. A method as claimed in claim 1, substantially as described in the Example.

17. A metal surface whenever prepared by a method as claimed in any of claims 1 to 16.

18. A conveyor belt the metal surface of which has been prepared by a method as claimed in any of claims 1 to 16.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43, Bloomsbury Square,
London : WC1A 2RA.

for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.